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Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water near a Fluorochemical Production Plant in the Netherlands

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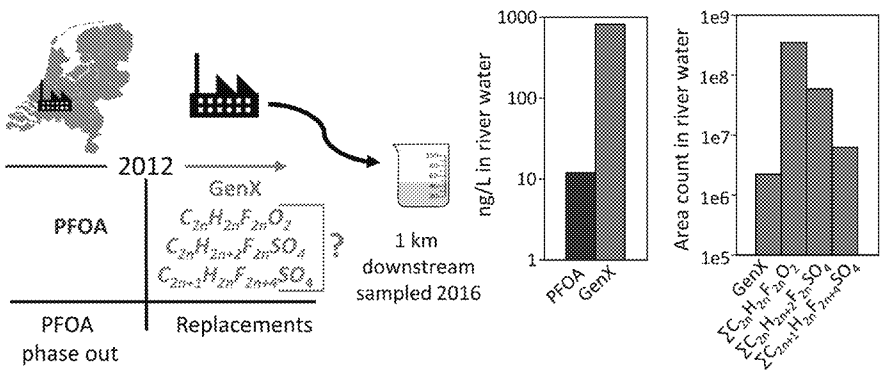
Supporting Information



ABSTRACT: The present study investigated the presence of legacy and emerging per- and polyfluoroalkyl substances (PFASs) in river water collected in 2016 up- and downstream from a fluorochemical production plant, as well as in river water from control sites, in The Netherlands. Additionally, drinking water samples were collected from municipalities in the vicinity from the production plant, as well as in other regions in The Netherlands. The PFOA replacement chemical GenX was detected at all downstream river sampling sites with the highest concentration (812 ng/L) at the first sampling location downstream from the production plant, which was 13 times higher than concentrations of sum perfluoroalkylcarboxylic acids and perfluoroalkanesulfonates (∑PFCA+∑PFSA). Using high resolution mass spectrometry, 11 polyfluoroalkyl acids belonging to the $C_{2n}H_{2n}F_{2n}O_2$, $C_{2n}H_{2n+2}F_{2n}SO_4$ or $C_{2n+1}H_{2n}F_{2n+4}SO_4$ homologue series were detected, but only in downstream water samples. These emerging PFASs followed a similar distribution as GenX among the downstream sampling sites, suggesting the production plant as the source. Polyfluoroalkyl sulfonates ($C_{2n}H_2F_{4n}SO_3$) were detected in all collected river water samples, and therefore appear to be ubiquitous contaminants in Dutch rivers. GenX was also detected in drinking water collected from 3 out of 4 municipalities in the vicinity of the production plant, with highest concentration at 11 ng/L. Drinking water containing the highest level of GenX also contained two $C_{2n}H_{2n}F_{2n}O_2$ homologues.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are industrial chemicals that are produced for numerous industrial and consumer products.[1] Due to their chemical properties, historically produced PFASs such as perfluoroalkylcarboxylic acids (PFCAs) and perfluoroalkanesulfonates (PFSAs) are classified as persistent, bioaccumulative and/or toxic chemicals. The production of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) (and their precursors) has been phased out by main producers in North America and Europe. PFCAs and PFSAs are global environmental contaminants and are found in the abiotic and biotic environment.[2−4]

Since the phase out of PFASs such as PFOS, PFOA, and their precursors, industry has shifted production to shorter chain length PFSAs and PFCAs and other replacement chemicals such as perfluoroalkyl ether acids (e.g., GenX).[5,6] Emissions from production plants are a direct source of fluorochemicals into the environment, and with the use of high resolution mass spectrometry (HRMS), several studies have reported on the presence of replacement PFASs in wastewater from manufacturing sites or in river water collected downstream from them, with concentrations estimated in the μg/L range.[7−10] Emerging PFASs detected in these studies included perfluoroalkyl (mono and poly) ether carboxylic acids including GenX (also named PFPrOPrA or HFPO−DA), polyfluoroalkyl carboxylic acids ($C_{2n}H_{2n}F_{2n}O_2$ homologues), and polyfluorinated alkanesulfonates and sulfates (see Supporting Information (SI) Table S7 for proposed chemical structures).

In The Netherlands, a fluorochemical production plant near the city of Dordrecht historically used PFOA until 2012, but is

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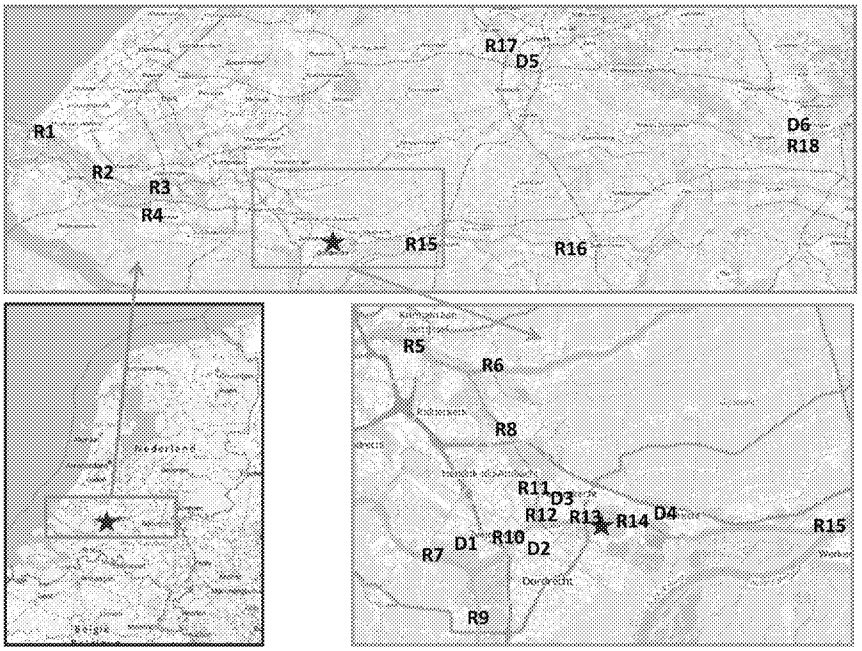

Figure 1. Sampling locations of river water samples (R1–R18) and drinking water samples (D1–D6) collected in The Netherlands in 2016. See SI Table S2 for more sample location details. The location of the fluorochemical production plant is indicated by the red star.

currently using the PFOA replacement GenX to produce fluoropolymers.[11] A previous study reported on the presence of GenX in Dutch river water collected ~50km downstream from the production plant in 2013 at 91 ng/L (12 times higher than PFOA concentrations).[12,13] However, to our knowledge no other measurements have been reported in Dutch water bodies. In the U.S., GenX concentrations downstream from a production site reached concentrations in the low μg/L range.[8] It is unclear what concentrations of GenX are present in the river close to the production plant in The Netherlands, and/or if also other emerging PFASs are currently being used and emitted to the local environment.

In the western part of The Netherlands, where the fluorochemical production plant is located, river water is used as the source for drinking water.[14] Studies have shown that drinking water treatment plants (DWTP) fail to completely remove legacy PFASs (PFCAs and PFSAs) during the process to produce drinking water.[15,16] This was recently also shown for GenX, where raw water and finished water contained comparable concentrations.[8] The presence of GenX in river water downstream from the Dordrecht fluorochemical production plant,[12] plus the fact that DWTPs poorly remove GenX, raises the question of whether GenX (and other emerging PFASs) could be present in drinking water in The Netherlands and thus be a source for human exposure.

Therefore, the objective of this study was to investigate the presence of GenX and other emerging PFASs in river water near the fluorochemical production plant by performing target analysis and suspect-screening for emerging PFASs reported in the literature. River water was collected from 18 locations, both upstream and downstream from the production plant. Target analyses and suspect-screening were also performed on drinking water samples collected from four cities in the vicinity of the plant and from two cities in central and eastern Netherlands (controls).

MATERIALS AND METHODS

Chemicals and Reagents. Target PFASs included $C_{4,6,7,8}$ PFSAs, C_{4-10} PFCAs, ADONA, and 6:2 Cl-PFESA were all obtained from Wellington laboratories (Guelph, ON, Canada), while GenX was obtained from Apollo Scientific (Cheshire, UK). A total of 11 isotopically labeled internal standards (SI Table S1) and recovery standards ($^{13}C_8$–PFOS and $^{13}C_8$–PFOA) were used, all obtained from Wellington Laboratories. All solvents and reagents used were of the highest purity commercially available.

Sample Collection and Preparation. A total of 18 river water samples were taken in October 2016 (Figure 1, SI Table S2). These included 13 samples taken downstream from the production plant (R1–R13), three samples taken upstream (R14–R16), and two samples taken from different waterbodies as control sites (R17–R18). Drinking water samples were taken at city halls in the municipalities close to the production plant (D1–D4), at a residential home in Utrecht (D5), and at RIKILT in Wageningen (D6) (Figure 1, SI Table S2). All river and drinking water samples were stored in prerinsed 1 L high-density polyethylene (HDPE) bottles at 4 °C until chemical analysis. Field blanks were taken by filling HDPE bottles with Milli-Q water and stored under the same conditions as the river and drinking water samples. The water sample preparation and LC-MSMS analysis is based on previous studies.[4,14] Briefly, a volume of 250 mL water was spiked with internal standards and loaded onto a WAX SPE cartridge (Waters; 3 mL, 60 mg) preconditioned with 4 mL methanol and 4 mL water. The SPE was subsequently washed with 4 mL sodium acetate buffer (pH 4) and 2 mL methanol. All target compounds were then eluted with 3 mL 2% NH_4OH in acetonitrile, and subsequently evaporated under a stream of nitrogen until dryness. The extract was redissolved in 300 μL acetonitrile and 675 μL 2 mM ammonium acetate in water and sonicated for 5 min. To a volume of 475 μL of this extract, 25 μL recovery standard ($^{13}C_8$–PFOS and $^{13}C_8$–PFOA at 100 pg/μL) was added and filtered prior to LC-MSMS analysis.

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Table 1. Concentrations (ng/L) of Detected PFASs in River (R) and Drinking (D) Water Collected in the Netherlands[a]

sampling number[b]	sample type (R)/ City (D)	GenX	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFHpS	PFOS	∑PFAS incl. GenX	∑PFAS excl. GenX
R1	downstream	48	5.3	<4	4.0	1.5	3.6	0.52	0.26	16	1.8	0.095	2.7	83	36
R2	downstream	58	4.6	4.1	4.3	1.5	3.7	0.49	0.26	18	1.5	0.11	2.9	100	42
R3	downstream	48	7.2	8.2	4.0	1.7	3.8	0.55	0.32	19	1.8	0.14	2.8	97	49
R4	downstream	14	6.1	6.8	5.6	2.0	3.9	0.53	0.23	23	1.9	0.10	2.8	67	53
R5	downstream	271	9.0	4.3	5.8	2.2	4.2	0.59	0.38	22	2.0	0.13	3.1	324	54
R6	downstream	433	8.1	4.5	5.6	1.8	4.8	0.70	0.41	20	2.1	0.17	3.6	485	52
R7	downstream	6.3	7.2	4.5	5.2	1.8	3.5	0.66	0.40	23	2.1	0.17	3.0	58	52
R8	Downstream	178	7.6	5.0	5.7	2.0	4.2	0.65	0.53	18	2.1	0.16	3.6	228	50
R9	downstream	1.7	10	4.5	5.8	1.7	3.7	0.66	0.38	25	1.9	0.12	3.1	59	57
R10	downstream	196	13	<4	5.3	1.6	4.7	0.71	0.36	27	2.2	0.16	2.9	254	58
R11	downstream	108	5.7	4.1	6.0	2.1	3.8	0.76	0.53	18	2.0	0.16	4.0	155	47
R12	downstream	144	5.3	4.7	6.4	2.0	4.2	1.0	0.80	18	2.0	0.20	6.5	195	51
R13	downstream	812	12	<4	5.7	2.2	12	0.84	0.52	26	2.2	0.11	3.2	876	65
R14	upstream	22	5.0	4.1	6.2	2.0	3.2	0.92	0.86	18	2.1	0.19	7.1	72	50
R15	upstream	<0.2[c]	4.1	5.2	6.3	1.9	3.0	0.78	0.45	20	2.0	0.13	4.1	49	49
R16	upstream	<0.2	10	9.2	6.0	1.8	2.8	0.54	0.38	21	2.2	0.17	3.1	57	57
R17	control site	<0.2	7.4	<4	5.1	1.9	3.0	1.0	0.41	12	2.0	0.15	4.1	38	38
R18	control site	<0.2	14	4.3	6.4	2.2	2.9	0.80	0.36	22	1.7	0.13	3.3	58	58
D1	Zwijndrecht	0.25	<2	5.7	5.3	2.4	2.7	0.28	0.10	3.4	0.40	0.021	0.40	21	21
D2	Dordrecht	0.48	<2	5.7	4.7	2.1	2.2	0.25	0.06	3.4	0.43	0.030	0.41	20	19
D3	Papendrecht	11	13	<4	2.9	1.1	11	0.09	<0.03	19	0.39	0.023	0.31	58	47
D4	Sliedrecht	<0.2	<2	<4	0.29	<0.05	<0.3	<0.03	<0.03	2.3	0.12	<0.02	0.054	2.7	2.7
D5	Utrecht	<0.2	<2	<4	0.27	<0.05	0.63	<0.03	<0.03	1.0	0.08	<0.02	0.080	2.1	2.1
D6	Wageningen	<0.2	<2	<4	<0.1	<0.05	<0.3	<0.03	<0.03	0.54	0.02	<0.02	<0.03	0.56	0.56

[a]ADONA and 6:2 Cl-PFESA were not detected in any of the samples. [b]See SI Table S2 and Figure 1 for more details on sampling locations; R = river water, D = drinking water. [c]Concentration was below the MQL.

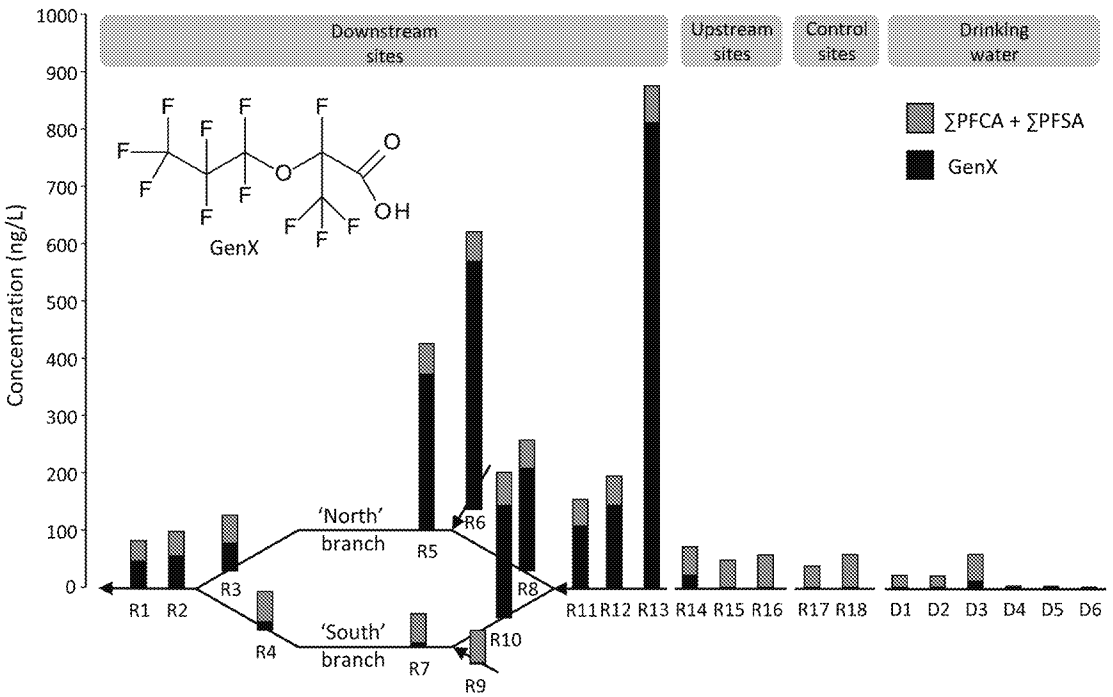

Figure 2. Concentrations of GenX and ∑PFCA (C_{4-10}) + ∑PFSA ($C_{4,6,7,8}$) in ng/L in river water samples (R1−R18) and drinking water samples (D1−D6) collected in 2016 in The Netherlands. Downstream from sampling site R11 the river splits into a "north" and "south" branch, which merge upstream from sampling site R2. Samples from R6 and R9 are collected from rivers merging with "north" or "south" branch. See Table 1 for individual PFCA and PFSA concentrations, and SI Table S2 and Figure 1 for locations of the sampling sites. The fluorochemical production plant is located between sampling sites R13 and R14, and the arrows indicate the general water flow direction.

Target Analysis. Target analysis was performed on a Shimazdu Nexera X2 LC-30AD UHPLC (Canby), connected to an AB Sciex Qtrap 5500 triple quadrupole mass spectrometer. Target compounds were separated on an Acquity UPLC BEH C18 column (Waters; 2.1 × 50 mm, 1.7 μm) and the column was kept at 35 °C. See SI Table S3 for details on

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

mobile phases and gradient program. Electrospray ionization in negative mode (ESI^-) was used and the ion spray voltage was set at −4500 V. The ion source temperature was set at 350 °C. For each target compound two fragments were monitored with optimized MS/MS parameters (see SI Table S1). Quantification was performed using an isotope dilution approach. Analytes lacking an analogous labeled standard were quantified using the internal standard with the closest retention time (SI Table S1). Quantification was performed using the precursor-product ion multiple reaction monitoring (MRM) transitions reported in SI Table S1. Calibration curves dissolved in water/acetonitrile (70/30), consisting of minimal 9 standards (range 0.05−25 ng/mL), were linear over the whole concentration range with r^2 values greater than 0.99. Besides the field blank, method blanks and spiked water samples were included during the analyses. For compounds where blank contamination was observed, the method quantification limits (MQLs) were determined as the mean plus three times the standard deviation of the quantified procedural blank signals. A blank correction was performed by subtracting the average quantified concentration in the blanks from PFAS concentrations in the samples. For other compounds the MQL was determined as the concentration calculated in a sample giving a peak with a signal-to-noise ratio of 10. SI Table S4 lists all compound-specific MQLs (ranging from 0.01 to 4 ng/L depending on the chemical) and recoveries of native PFASs spiked to water at 3 different concentrations (ranging from 81 to 115% depending on the chemical and spiking concentrations). Internal standard recoveries in the river and drinking water samples are listed in SI Table S5 and ranged from 46 to 108% depending on the internal standard.

Suspect-Screening Analysis. Suspect-screening was performed on an Ultimate 3000 UPLC system connected to an QExactive Orbitrap high resolution mass spectrometer (HRMS) (Thermo Scientific, CA). An Atlantis T3 column (3 μm particles, 100 × 3 mm; Waters) was used for compound separation. See SI Table S6 for details on mobile phases and gradient program. The QExactive was operated in negative electrospray ionization (ESI^-) mode in full scan (100−1250 m/z) at a resolution of 140,000. The capillary voltage was set at 2.5 kV, and the capillary and heater temperatures were set at 250 and 400 °C, respectively. MS/MS experiments were performed in order to obtain fragment information for structural confirmation. The combined fragments obtained at collision energies of 20 and 80 eV were detected by the QExactive mass analyzer at a resolution of 35 000. Samples were screened for a database of compounds reported in the literature[7−10] and potential other homologues differing CF_2 (49.9968), CF_2CH_2 (64.0124), or CF_2O (65,9917) in mass.

RESULTS AND DISCUSSION

Legacy PFASs in River and Drinking Water. Of the legacy PFASs (C_{4-10} PFCAs and $C_{4,6,7,8}$ PFSAs), PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFHpS, and PFOS were detected in the river water samples (Table 1). Concentrations of the sum PFCAs and PFSAs were quite consistent among all the samples and ranged from 36 to 65 ng/L (Table 1, Figure 2). Also the sum concentrations from the control sites (R17 and R18) fell within this range. Highest concentrations of individual PFASs were observed for PFBS, ranging between 12 and 27 ng/L, followed by PFBA, PFPA, PFHxA, PFOA, and PFOS with a comparable concentration range, that is, 2.7−14 ng/L. Concentration of PFOA in the first sampling site downstream from the production plant (R13) was 2.5−4.4 times higher compared to the other sampling sites even though production of PFOA ceased in 2012. The pattern of detected PFCAs and PFSAs was comparable for all river water samples and was dominated by shorter chain PFASs (SI Figure S1). The dominant PFAAs were PFBS, PFBA, and PFHxA and contributed on average 40%, 15%, and 11% to ∑PFAA, respectively, which was significantly higher ($p < 0.0001$) compared to other PFAAs. Earlier studies reported legacy PFAS concentrations in river water taken from similar sampling sites in 2008 and 2013,[12,13,17] and ∑PFCA+PFSA concentrations have declined from 2008 to 2013, whereas the concentrations are similar between 2013 and 2016 (present study) (SI Figure S2). Also, PFOA concentrations taken at a sampling location downstream in 2008 (when PFOA was still produced), contained elevated PFOA concentrations (~34 ng/L) compared to other locations.[17] Such high PFOA concentrations were not observed in the present samples.

In the drinking water samples, concentrations of the legacy PFASs (C_{4-10} PFCAs and $C_{4,6,7,8}$ PFSAs) were more variable among the sampling locations compared to the river water samples, and ranged from 0.56 to 47 ng/L (Table 1). The highest sum concentration was found in drinking water from Papendrecht (D3) followed by Zwijndrecht/Dordrecht (D1/D2), and lower concentrations in drinking water from Sliedrecht (D4), Utrecht (D5), and Wageningen (D6). In the most contaminated drinking water samples (D1−D3), the PFCA/PFSA pattern was dominated by the shorter chain length PFBA, PFPA, PFHxA, PFBS (69−72% of sum concentrations), while in drinking water samples D4−D6 the pattern was dominated by PFOA and PFBS (79−96% of sum concentrations). Several studies have reported on the presence of PFASs in drinking water in The Netherlands.[14,18] Zafeiraki et al.[14] reported on concentrations in drinking water collected from several cities in The Netherlands. Drinking water collected from the west of The Netherlands (sourced by river water) had higher concentrations compared to the east (sourced by groundwater). Drinking water samples D1−D3 had comparable concentrations to earlier reported concentrations in water collected in the west of The Netherlands, while D5 and D6 had lower concentrations.[14] Although being geographically close to the sampling locations D1−D3, drinking water collected from Sliedrecht (D4) had lower concentrations than the three other nearby cities. This can be explained by the fact that the source of the drinking water for Sliedrecht originates from central Netherlands, where groundwater is used instead of river water.[14]

Emerging PFASs Detected Downstream from the Fluorochemical Production Plant. Target analyses of the emerging PFASs GenX, ADONA, and 6:2 Cl-PFESA were performed on the river water samples. GenX was the only detected emerging PFAS in 78% of the river water samples, while ADONA and 6:2 Cl-PFESA were below the detection limit in all samples. Suspect-screening analysis showed the presence of several emerging PFAS homologue groups in river water samples downstream from the fluorochemical production plant. Emerging PFASs with chain lengths of varying CH_2CF_2 units were detected in the following homologue series: $C_{2n}H_{2n}F_{2n}O_2$, $C_{2n}H_{2n+2}F_{2n}SO_4$, and $C_{2n+1}H_{2n}F_{2n+4}SO_4$.

GenX. In river water samples, detectable GenX concentrations ranged from 1.7 to 812 ng/L (Table 1). GenX was detected at all sampling sites downstream from the production plant, with the highest concentrations at the first sampling site

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

Table 2. Summary of Detected Emerging PFASs in River and Drinking Water Collected in the Netherlands

homologue	proposed structure	observed mass (m/z)	ppm error	detection in river water[a]		detection in drinking water[a]	literature reporting
				downstream	upstream/ control		
$C_nHF_{2n-1}O_3$	$C_6HF_{11}O_3$ (GenX)[b]	328.9678	0.30	R1–R13	R14	D1- Zwijndrecht D2 - Dordrecht D3 - Papendrecht	river water – U.S./ Netherlands/China[7,8,12]
$C_{2n}H_{2n}F_{2n}O_2$	$C_6H_6F_6O_2$[c]	223.0200	0.17	R1–R8,10–13	R14	D3 - Papendrecht	river water – U.S.[9]
	$C_8H_8F_8O_2$[c]	287.0325	0.28	R1–R8,10–13	R14		river water – U.S.[9]
	$C_{10}H_{10}F_{10}O_2$[c]	351.0450	0.59	R1–R8,10–13	R14	D3 - Papendrecht	river water – U.S.[9]
	$C_{12}H_{12}F_{12}O_2$[c]	415.0577	0.89	R1–R8,10–13	R14		river water – U.S.[9]
	$C_{14}H_{14}F_{14}O_2$	479.0701	0.76	R1–R6,8,1–13	R14		river water – U.S.[9]
	$C_{16}H_{16}F_{16}O_2$	543.0822	0.01	R1–R3,5,6,8,10–13	R14		River water – U.S.[9]
$C_{2n}H_{2n+2}F_{2n}SO_4$	$C_4H_6F_4SO_4$[c]	224.9850	0.00	R1–R6,8,10–13			river water – U.S.[9]
	$C_6H_8F_6SO_4$[c]	288.9976	0.06	R1–R3,5,6,8,10–13			
$C_{2n+1}H_{2n}F_{2n+4}SO_4$	$C_5H_4F_8SO_4$	310.9631	0.41	R1–R3,5,6,8,10–13			wastewater – China[10]
	$C_7H_6F_{10}SO_4$	374.9755	0.19	R5,10,13			
	$C_9H_8F_{12}SO_4$	438.9879	0.04	R5,6,8,10–R13			
$C_{2n}H_2F_{4n}SO_3$	$C_4H_2F_8SO_3$	280.9523	−0.36	R1–R13	R14–R18	D3 - Papendrecht D4 - Sliedrecht	river water – U.S.[9]
	$C_6H_2F_{12}SO_3$	380.9462	0.48	R10,13			

[a]See SI Table S2 and Figure 1 for more details on sampling locations. [b]Confirmed with an authentic standard. [c]Multiple peaks (isomers) were detected, observed mass and ppm error are average values.

downstream from the production plant (R13) (Figure 2). Detectable concentrations were measured in the upstream sampling site R14 (1 km upstream from the production plant), as well as at site R6 (just upstream on the river Lek before merging with the river "Noord" (R8)). Tidal changes in the North Sea can influence the flow of the water in the studied area,[19] and could explain GenX being detected at sampling locations R6 and R14. Also, it remains unclear at what exact location wastewater is discharged into the river. Sampling site R14 could potentially be close to this discharge point resulting in lower, but detectable concentrations. At sampling locations further upstream from the production plant (R15 and R16) and the control sites (R17 and R18) no GenX was detected. When detected, GenX concentrations were 0.03–13 times the concentration of sum-PFSA/PFCA concentrations (Figure 2). A previous study reported on the presence of GenX in river water downstream (collected in 2013) from the production plant and among similar sampling locations, a comparable distribution of GenX concentrations was found.[12,13] A site close to R2 contained 91 ng/L, which was slightly higher than the presently found concentration at that location (58 ng/L), while at sites close to R7 and R15 GenX was not detected (in present sample R7 it is 6 ng/L and in R15 < MQL). In the U.S., GenX was detected in river water used as a source for a drinking water treatment plant (DWTP) and collected downstream from a manufacturing plant on the Cape Fear River, while it was not detected in water samples collected upstream.[8] In that study, average GenX concentrations in the downstream samples were approximately 600 ng/L, which was 8 times higher compared to the sum PFSA/PFCA concentrations. Strynar et al.[7] and Sun et al.[8] reported on the presence of other perfluoroalkyl ether carboxylic acids in river water, however, these emerging PFASs were not detected in the present samples.

A general declining trend in the GenX concentrations was seen with the highest concentration at the first sampling location downstream from the production plant and low concentrations at the sampling location at the mouth of the river flowing into the North Sea, although this declining trend was not consistent for all sites (Figure 2). Several kilometres downstream from the production plant, the river splits into a "north" and "south" branch, with comparable concentrations in the first sampling sites after the split (sites R8 and R10). Further sampling downstream in the branches showed that generally higher concentrations were seen in the river water collected from the "north" branch compared to the "south" branch. There are several factors that could have played a role in the distribution of GenX concentrations downstream from the production plant. As described above, tidal changes could have influenced the river flow and therefore possibly the GenX concentrations. Second, it remains unclear at what frequency and duration wastewater is discharged into the river, and third, the river water samples were collected over 2 days (see SI Table S2), which could be an important factor when there are day-to-day differences in wastewater discharge into the river.

$C_{2n}H_{2n}F_{2n}O_2$, $C_{2n}H_{2n+2}F_{2n}SO_4$, and $C_{2n+1}H_{2n}F_{2n+4}SO_4$ Homologue Series. A series of chromatographic peaks were detected in river water samples with increasing masses of 64.0124 amu (i.e., CH_2CF_2) (Table 2). Newton et al.[9] reported on the presence of peaks with the same masses in river water downstream from manufacturing facilities in the U.S. and identified these peaks as polyfluorinated carboxylic acids with the chemical structure $C_{2n}H_{2n}F_{2n}O_2$. In the present river water samples, peaks were detected with masses corresponding to $C_{2n}H_{2n}F_{2n}O_2$ homologues with n = 3, 4, 5, 6, 7, and 8 (Table 2, SI Figure S3). In a mass defect plot (generated according to Newton et al.[9]) the chemicals within this homologue group

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Environ. Sci. Technol. XXXX, XXX, XXX–XXX

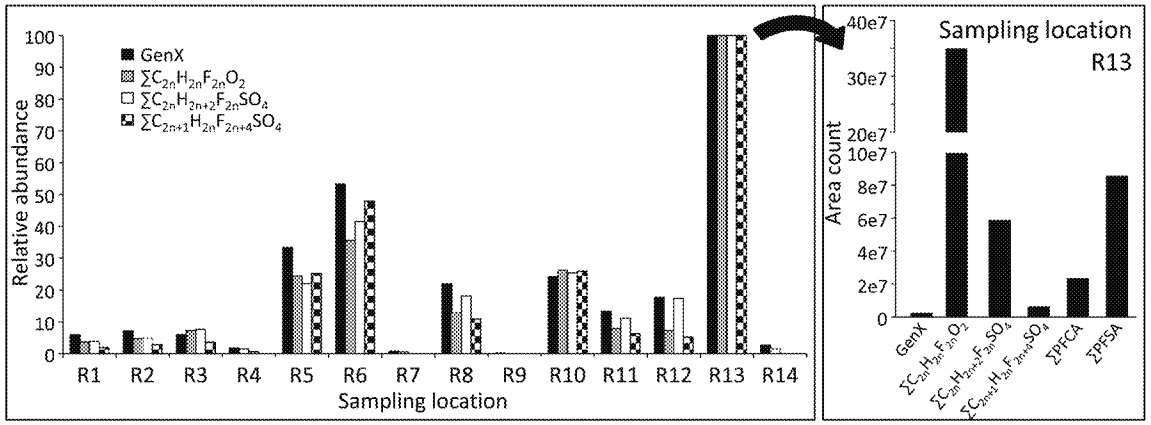

Figure 3. Relative HRMS instrumental response (with instrumental response at sampling location R13 set at 100%) of detected emerging PFAS homologue series in river water sampled downstream from a fluorochemical production plant (R15–R18 contained no detectable peaks of the homologue series) (left plot), and HRMS area count of emerging and legacy homologue series at sampling location R13 (right plot). See Tables 1 and 2 for individual compounds detected within a homologue series, and SI Table S2 and Figure 1 for more details on sampling locations. The fluorochemical production plant is located between sampling sites R13 and R14.

showed similar mass defects relative to their mass (SI Figure S4). For $C_6H_6F_6O_2$, $C_8H_8F_8O_2$, $C_{10}H_{10}F_{10}O_2$, and $C_{12}H_{12}F_{12}O_2$ two or three peaks were detected representing structural isomers. Experimental masses of the (isomer) peaks were within 1 ppm of the theoretical mass. MS/MS mass spectra of the homologue series showed similar fragments as described by Newton et al.[9] whereby a loss of 63.9960 amu (CO_2HF) and consecutive losses of 20.0060 amu (HF) were observed (SI Figure S3). Possible structures of the detected chemicals provided by Newton et al.[9] can be found in SI Table S7. In the river water samples the pattern of $C_{2n}H_{2n}F_{2n}O_2$ homologue series (when detected) was quite consistent and dominated by $C_6H_6F_6O_2$ and $C_{10}H_{10}F_{10}O_2$ (based on area count; SI Figure S5). This was consistent with the pattern detected by Newton et al.[9] The detection of the $C_{2n}H_{2n}F_{2n}O_2$ homologue series in the river water samples was exclusively in samples taken downstream from the production plant (with the exception of location R14, which can be explained by tidal influences as described above). Based on total $C_{2n}H_{2n}F_{2n}O_2$ homologue area count, these polyfluorinated carboxylic acids followed the same distribution as GenX when comparing downstream sampling locations (Figure 3), indicating the production facility as a source of these polyfluorinated carboxylic acids into the environment. Strong correlations (r^2-values > 0.96) were observed between the individual homologues among the sampling locations further strengthening that these chemicals originate from the same source. Instrumental responses of the detected polyfluorinated carboxylic acids surpassed the responses of the perfluorinated carboxylic acids with the same chain length (e.g., $C_6H_6F_6O_2$ vs PFHxA). At sampling location R13 (first sampling locations downstream), $C_6H_6F_6O_2$, $C_8H_8F_8O_2$, and $C_{10}H_{10}F_{10}O_2$ exceeded the PFHxA, PFOA, and PFDA area count by a factor of 36, 5, and 4600, respectively. Assuming comparable instrumental responses between these per- and polyfluorocarboxylic acids, concentrations of $C_6H_6F_6O_2$, $C_8H_8F_8O_2$, and $C_{10}H_{10}F_{10}O_2$ in sample R13 would be in the range of 200, 60, and 2400 ng/L, respectively. Using this approach, Newton et al.[9] estimated that concentrations of polyfluorocarboxylic acids could exceed 1 μg/L in U.S. river water downstream from manufacturing facilities.

Two chromatographic peaks at 224.9850 *m/z* were detected in river water samples (Table 2, SI Figure S6), which coincided with the detection of a peak at this mass by Newton et al.[9] They predicted the formula $C_4H_6F_4SO_4$ and provide two possible structures, which could coincide with the two peaks detected in the present samples. At 288.9976 *m/z* 2 peaks were found in the river water samples, differing 64.0126 amu (CH_2CF_2) with $C_4H_6F_4SO_4$. In a mass defect plot both these chemicals within this homologue group showed to have similar mass defects relative to their mass (SI Figure S4). Mass spectra for both these parent masses contained peaks at consecutive losses of HF and showed the presence of 79.9574 amu (SO_3^-) and 96.9601 (SO_4H^-) (SI Figure S6). For 224.9850 *m/z* the mass spectra contained the same fragments as reported earlier.[9] Given the similarity in mass spectra between 224.9850 *m/z* and 288.9976 *m/z*, a proposed structure for 288.9976 *m/z* is $C_6H_8F_6SO_4$, thus both chemicals belonging to the $C_{2n}H_{2n+2}F_{2n}SO_4$ homologue group. Possible structures of the detected chemicals, as provided by Newton et al.,[9] can be found in SI Table S7. Both compounds were detected in almost all downstream river samples (R1–R13), while they were not detected in upstream or control sampling sites (Table 2). Signal intensities of $C_4H_6F_4SO_4$ and $C_6H_8F_6SO_4$ were strongly correlated among the sampling locations (r^2 = 0.981), with areas of $C_4H_6F_4SO_4$ being about 2 times higher as for $C_6H_8F_6SO_4$. Sum area of this homologue group followed the same distribution among the downstream sampling locations as GenX and the $C_{2n}H_{2n}F_{2n}O_2$ homologue groups (Figure 3). At the first sampling location downstream from the production plant (R13), signal intensities of this homologue group were 27 times higher as for GenX, but about 6 times lower compared to the $C_{2n}H_{2n}F_{2n}O_2$ homologue series (Figure 3).

Peaks at 310.9631, 374.9755, and 438.9879 *m/z* were detected in the downstream river water samples (R1–R13; Table 2, SI Figure S7). Liu et al.[10] reported on the presence of chemicals with these masses in wastewater from a fluorochemical manufacturing park in China, and proposed the general formula $C_{2n+1}H_{2n}F_{2n+4}SO_4$ for this homologue series. In a mass defect plot all three chemicals within this homologue group showed to have similar mass defects relative to their mass (SI Figure S4). The masses of the three peaks would correspond to $C_5H_4F_8SO_4$, $C_7H_6F_{10}SO_4$, and $C_9H_8F_{12}SO_4$ with a mass error of <0.5 ppm. Liu et al.[10] provided detailed MS/MS spectra for $C_9H_8F_{12}SO_4$ and fragments including 79.9573 amu (SO_3^-),

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Environ. Sci. Technol. XXXX, XXX, XXX–XXX

96.9601 amu (SO_4H^-), 190.9926 amu ($C_8F_5^-$), and 418.9827 amu ($C_9H_6F_{11}SO_4$) were detected in the present samples (SI Figure S7). Signal intensities in de MS/MS spectra for $C_5H_4F_8SO_4$ and $C_7H_6F_{10}SO_4$ were lower compared to $C_9H_8F_{12}SO_4$, however, the SO_3^- and SO_4H^- fragments were detected for both compounds. Liu et al.[10] provided no possible structures for the detected chemicals, and also the present data provided no further information on the exact structure. Based on the parent mass, $C_5H_4F_8SO_4$ was the most abundant compound, followed by $C_9H_8F_{12}SO_4$ and $C_7H_6F_{10}SO_4$. All three chemicals were detected only in downstream sampling sites (varying from 3 to 10 out of 13 sites) and were not detected upstream from the manufacturing site or control sites. When detected, strong correlations were seen among the signal intensities of the three chemicals among the sampling locations (r^2-values ranging between 0.804 and 0.985). Based on the similarity in the distribution of this homologue series among the sampling locations compared to GenX and the above-mentioned emerging homologue series (Figure 3), it appears that $C_{2n+1}H_{2n}F_{2n+4}SO_4$ based chemicals are emitted by the fluorochemical production plant. At the first sampling location downstream from the production plant (R13), signal intensities of this homologue group were approximately 3 times higher as for GenX, but almost 10 times lower compared to the $C_nH_{n+2}F_nSO_4$ homologue series (Figure 3).

Emerging PFASs Detected at All River Sampling Sites. A chromatographic peak at 280.9526 m/z was detected in all the river water samples (Table 2, SI Figure S8). Newton et al.[9] found a peak with this mass in river water downstream from a manufacturing facility in the U.S., and proposed it to be a chemical with the formula $C_4H_2F_8SO_3$, and reported it as an impurity in the production of PFBS. A similar MS/MS fragmentation pattern was observed as reported earlier[9] with 79.9574 m/z (SO_3^-) and 98.9557 m/z (SO_3F^-) as the dominant fragments (SI Figure S8), and a possible structure of the detected chemical, as provided by Newton et al.,[9] can be found in SI Table S7. $C_4H_2F_8SO_3$ was detected in the upstream, downstream, and control river samples with comparable signal intensities. The fluorochemical production plant in the studied area appears not to be a source of this chemical in the studied rivers. Being structurally similar to PFBS, a strong positive correlation (r^2 = 0.958) was observed between the PFBS area count and $C_4H_2F_8SO_3$ area count in the river water samples. Area count of $C_4H_2F_8SO_3$ was systematically lower compared to PFBS area count in the river samples by a factor of 24. Assuming PFBS and $C_4H_2F_8SO_3$ have similar instrumental responses, estimated concentrations would be below 1 ng/L. Newton et al.[9] reported concentrations of $C_4H_2F_8SO_3$ in the 100−1000 ng/L range, however, in that study samples were taken downstream from a manufacturing facility. That same study reported on the detection of structural homologues of $C_4H_2F_8SO_3$ differing CH_2CF_2 unit, however, these homologues were not detected.[9] On the other hand, a chromatographic peak at 380.9462 m/z was detected in samples R10 and R13 which could be a potential homologue of $C_4H_2F_8SO_3$, differing $(CF_2)_2$ units in structure (SI Figure S8). Both chemicals had a similar mass defect relative to their mass (SI Figure S4). Signal intensities of this peak were 12 and 45 times lower compared to the intensity of $C_4H_2F_8SO_3$ when detected in the samples, therefore, for this peak only the SO_3^- fragment (79.9574 m/z) was observed in the MS/MS spectra. A proposed structure for this peak could be $C_6H_2F_{12}SO_3$. The signal intensity of this chemical was 20 times lower compared to the structurally similar PFHxS, and assuming similar instrumental responses the estimated concentration of $C_6H_2F_{12}SO_3$ would be <0.1 ng/L.

Emerging PFASs in Drinking Water. GenX was detected in drinking water collected from the cities Zwijndrecht, Dordrecht, and Papendrecht (D1−D3) with concentrations ranging from 0.25 to 11 ng/L, while drinking water from Sliedrecht, Utrecht, and Wageningen (D4−D6) did not contain detectable GenX (Table 1). The source of the drinking water (river or groundwater) as described above, could explain this difference. River water originating close to the sampling site R6 is used for drinking water production for Papendrecht, GenX was detected at R6 at elevated concentrations (Figure 2). Drinking water from Zwijndrecht (D1) and Dordrecht (D2) contained GenX concentrations <1 ng/L. The majority of the drinking water for these cities is sourced by water from the river Maas, however, groundwater from the Dordrecht-region is also used (possible containing GenX). This could explain the lower but detectable concentrations. For the city of Sliedrecht, river water further upstream on the river Lek is used to produce drinking water. GenX concentrations at this location are expected to be low or not present (although not measured in this study). The data provide an indication that the local DWTPs were not able to (completely) remove GenX from drinking water. Information on drinking water contamination with GenX is limited, however, a recent study reported GenX in finished water from a DWTP to be almost 500 ng/L.[8] That study also showed that GenX concentrations in the raw water and at several treatment steps were comparable, indicating the poor removal of this emerging PFASs during drinking water treatment.

Two chemicals from the $C_{2n}H_{2n}F_{2n}O_2$ homologue series (i.e., $C_6H_6F_6O_2$ and $C_{10}H_{10}F_{10}O_2$) were only detected in drinking water sample D3 (Papendrecht) (Table 2). Using the same estimation approach as described for river water, concentrations of these two chemicals were <1 ng/L. Chemicals from the $C_{2n}H_{2n+2}F_{2n}SO_4$ and $C_{2n+1}H_{2n}F_{2n+4}SO_4$ homologue series were not detected in any of the drinking water samples. From the $C_{2n}H_2F_{4n}SO_3$ homologue series, only $C_4H_2F_8SO_3$ was detected in 2 drinking water samples (D3 and D4) (Table 2). Like in the river water samples, instrumental intensities of $C_4H_2F_8SO_3$ were lower compared to PFBS in the drinking water samples by a factor of about 10. Estimated $C_4H_2F_8SO_3$ concentrations would be ~1 ng/L in the highest drinking water sample (D3). To our knowledge, this is the first reporting on the presence of $C_6H_6F_6O_2$, $C_{10}H_{10}F_{10}O_2$, and $C_4H_2F_8SO_3$ in drinking water.

Implications for Environmental and Human Exposure to Emerging PFASs. Based on the findings of this study, the fluorochemical production plant is not only emitting GenX but also several other polyfluoroalkyl substances containing C−H bonds and varying in chain length by CF_2−CH_2 units with either a carboxylic acid or sulfate functional group. European production volumes of GenX are reported to be in the range of 10−100 tonnes per year,[20] however, no information could be found on production volumes and applications of the polyfluorinated homologues also detected in the river water.

In river water, concentrations of GenX exceeded ∑PFCA + ∑PFSA concentrations in 10 out of 13 sampling locations downstream from the production plant, with the highest concentration surpassing 800 ng/L. This could lead to elevated exposure of aquatic species downstream from the production plant compared to other locations upstream of the production plant. A laboratory study determined the bioconcentration factor (BCF) of GenX in common carp (*Cyprinus carpio*) and

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Environ. Sci. Technol. XXXX, XXX, XXX−XXX

estimated it to be <30 (based on 28-day exposure), however, dietary accumulation of GenX was not studied.[21] Future research on dietary accumulation of GenX in fish and/or sampling of aquatic species downstream from the production plant would provide more information on the bioaccumulation potential of GenX in these aquatic species and the behavior of GenX in aquatic food webs. Concentrations of chemicals within the $C_{2n}H_{2n}F_{2n}O_2$ homologue series were estimated to surpass the GenX concentrations in river water samples. Although these polyfluoroalkylcarboxylic acids appear to be more hydrophilic compared to the perfluoroalkylcarboxylic acids (e.g, water solubility of polyfluoroalkylcarboxylic acids is ≥10 times higher compared to same chain length perfluoroalkylcarboxylic acid; USEPA EPISuite, version 4.11), it remains unclear whether these chemicals possess persistent, bioaccumulative or toxic (PBT) properties. Especially aquatic species residing close to fluorochemical production plant wastewater effluent could be exposed to these chemicals in concentrations up to μg/L range as shown in the present study and in the U.S.[9] Chemicals in both polyfluoroalkyl sulfate homologue series appear to be less abundant in river water compared to $C_{2n}H_{2n}F_{2n}O_2$ homologues (based on instrumental response; Figure 3), however, information on PBT properties for these chemicals are lacking, and are needed in order to assess the potential risk for aquatic species.

Of the chemicals presumably emitted by the fluorochemical production plant, GenX, $C_6H_6F_6O_2$, and $C_{10}H_{10}F_{10}O_2$ were detected in drinking water collected from one or more cities, as well as $C_4H_2F_8SO_3$ (which appears to be an ubiquitous contaminant in Dutch rivers). The highest GenX concentrations were found in drinking water from Papendrecht (D3), and only in drinking water from this city $C_6H_6F_6O_2$, and $C_{10}H_{10}F_{10}O_2$ were detected. The higher abundance of these chemicals in Papendrecht compared to the other cities studied could be linked to the source of the drinking water (as described above). Regardless, the presence of these chemicals in drinking water may indicate that DWTPs that produced the drinking water are not capable of (completely) removing these chemicals during their treatment processes. For the city of Papendrecht, consumption of drinking water leads to a greater exposure to GenX, $C_6H_6F_6O_2$, and $C_{10}H_{10}F_{10}O_2$ of the local population compared to the other cities included in this study. The local population exposure to GenX via drinking water is estimated at 220 pg/kg/day (using the approach by Gebbink et al.[22]), which was comparable to the daily intake via drinking water of the chemical it replaced, that is, PFOA. Estimated daily intakes of shorter chain length PFCAs (C_{5-7}) via drinking water consumption for the locations D1−D3 were up to 270 pg/kg/day. Regardless, the sum concentration of detected PFASs in the Papendrecht drinking water sample did not exceed regulatory guidelines set by several provincial and national authorities (as summarized by Cousins et al.[23]). It should be noted that the number of drinking water samples in this study was limited, and more research is needed to confirm our findings. Although for PFOA multiple human exposure pathways have been identified, and the importance of drinking water is not the most important exposure pathway,[22] this is not known for GenX, or for $C_6H_6F_6O_2$ and $C_{10}H_{10}F_{10}O_2$. Major human exposure pathways, such as ingestion of food and dust, and inhalation of air need to be studied in order to assess the total human exposure and determine the relative importance of drinking water. Information on toxicokinetics of GenX such as absorption, distribution, metabolism and excretion (ADME) is extremely limited. Animal studies have shown a lower bioaccumulation potential of GenX compared to PFOA and GenX is not metabolized.[24] However, how fast humans eliminate GenX remains unclear. Concentrations of $C_6H_6F_6O_2$ and $C_{10}H_{10}F_{10}O_2$ were estimated to be lower than 1 ng/L, and therefore human exposure via drinking water would be lower (C_6) or comparable (C_{10}) relative to their perfluorinated homologues. To our knowledge, this is the first reporting of human exposure to these chemicals, but further research efforts should be made to investigate potential other human exposure pathways in order to get a more complete picture on the total human exposure.

Emerging PFASs were identified in river water and drinking water in The Netherlands, possibly linked to the presence of a fluorochemical production plant. However, other emerging PFAS homologues were detected in all collected river water samples, indicating sources other than the fluorochemical production plant near Dordrecht. GenX has been used since 2012 as a PFOA replacement and in 2017 emission permits issued by local authorities reduced the allowable amount of GenX that can be emitted via wastewater from 6400 to 2035 kg per year.[25] For the other detected homologue series it is unclear when production started and for what products they are used. Information on the production volumes and environmental occurrence of the emerging PFASs is extremely limited and more research is needed to better assess human and wildlife exposure to these chemicals. The availability of authentic standards for these emerging PFASs is essential in order to perform this research. The identification of drinking water as a human exposure pathway for a replacement PFAS (GenX) that has been in use only since 2012 emphasizes the need for more data on the environmental presence of other replacement PFASs that are only recently produced, and for which there is very limited information.[26]

■ ASSOCIATED CONTENT

Supporting Information

Tables (S1−S7) and Figures (S1−S8) addressing details on analytical methods and method performance, sample information, PFCA and PFSA patterns, and detection and identification of emerging homologue groups. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b02488.

(PDF)

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Notes

The authors declare no competing financial interest.

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